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CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION

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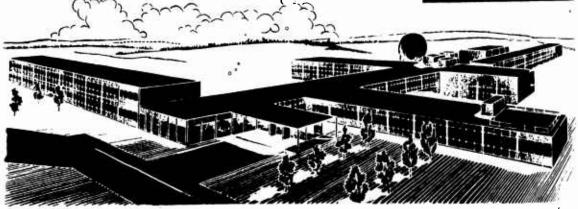
AEROCHEM RESEARCH LABORATORIES, INC. PRINCETON, NEW JERSEY



AUGUST 1961

AERONAUTICAL RESEARCH LABORATORY OFFICE OF AEROSPACE RESEARCH UNITED STATES AIR FORCE





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CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION

II. EXPERIMENTAL STUDIES OF HEAT TRANSFER FROM COMBUSTION GASES TO SOLID SURFACES

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FOREWORD

This work constitutes Part II of a two part final report covering theoretical and experimental aspects of the general problem of convective heat transfer with chemical reaction. Part I is directed toward the theoretical development of correlation formulae for the prediction of heat fluxes in high performance rocket motors and related systems. The research reported on herein deals with experimental studies of heat transfer from combustion gases to solid surfaces.

The author has benefited greatly from frequent discussion with Professor R. Eichhorn of Princeton University throughout the course of this research. It is also a pleasure to thank Professor J. Fenn for his initial guidance and Ted Douglass for his skill and persistence in carrying out the subatmospheric experiments. The contributions of Frank Kuehner, Donald Jost and Charlotte Phillips in the computational phases of this research are greatfully acknowledged. Joseph Shetz assisted with the assembly of the burner and mercury flow system. Thanks are due to Robert Zeh for his assistance with the explosion program instrumentation. Finally, the author particularly wishes to thank Dr. H. F. Calcote of this laboratory and Mr. Everett Stephens and Mr. Erich Soehngen, of the Aeronautical Research Laboratory, Office of Aerospace Research, for their technical interest and continued support.

ABSTRACT

A novel method of measuring steady state heat fluxes to strongly cooled catalytic and non-catalytic solids within subatmospheric flames is described and used to obtain heat flux data as a function of position in flat ethylene/air and hydrogen/oxygen flames stabilized on a 4 inch diameter burner.

For determining energy transport properties of gases at pressures up to or exceeding 1000 psi, a constant volume explosion technique is introduced. Factors limiting the attainable accuracy of emissivity and thermal diffusivity determinations are quantitatively discussed. In view of the theoretical potentialities of the technique, a series of preliminary explosion experiments have been carried out using stoichiometric hydrogen/oxygen mixtures in a cylindrical vessel.

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NOMENCLATURE

- a exponent appearing in Eq. (23)
- b exponent appearing in Eq. (23) •
- specific heat at constant pressure
- c, specific heat at constant volume
- d diameter
- D Fick diffusivity
- e specific internal energy
- E total internal energy in vessel
- g. gravitational acceleration at sea level
- Gr Grashof number, Eq.(18)
- L length over which coolant temperature rise is measured
- m mass flow rate
- m molecular weight
- n summation index, Eq.(11)
- Pr, Prandtl number for heat conduction = v/a
- total pressure
- q" heat transfer rate per unit area
- Q total heat transferred across boundary
- R bomb radius
- R universalegas constant
- S surface area of vessel walls
- t time
- T absolute temperature
- V enclosed volume within vessel
- α thermal diffusivity
- ullet eta coefficient of thermal expansion; 1/T for a perfect gas ullet
- Y specific heat ratio
- δ boundary layer thickness
- € * total hemispheric emissivity
- λ thermal conductivity of fluid or solid
- ν * kinematic viscosity of fluid
- ρ absolute density
- o Stefan-Boltzmann radiation constant
- τ nondimensional time

equivalence ratio (fuel to oxidizer ratio by volume or mass normalized by the corresponding stoichiometric ratio)
 e

Subscripts

- a apparent
- Hg pertaining to mercury
- f film
- k pertaining to species k
- m at the moment of maximum pressure
- o at initial condition (usually when ignition occurs)
- T partial derivative at constant temperature
- u universal
- w at the wall or pertaining to the solid
- ε pertaining to radiation
- λ pertaining to heat conduction
- ρ partial derivative at constant density
- crit critical

Superscripts

* normalized by the value of the total heat loss at $t = \infty$

Miscellaneous

- () average value of ()
- ∆ change in
- partial differential operator
- d ordinary differential operator
- exp() the exponential function e()

I. INTRODUCTION

It has been recognized for some time that energy transfer between gases and solid surfaces can be affected by thermochemical processes and, in particular, the kinetics of these processes 1,2,3. This may be viewed as either a blessing or a nuisance, depending on one's point of view. In either case, however, it is necessary to understand the magnitude of the effects to be expected, and the way in which these effects will change with changes in environmental conditions. The designer of those stationary power stations relying ultimately on the energy content of chemical fuels will always be interested in finding, understanding, and applying methods of increasing the efficiency and rates of energy transfer from reactant or product gases to heat exchanger surfaces. Similarly, thermochemical effects can govern the choice of gaseous coolants for such devices as nuclear reactors, high-current electrical generators, compact electromagnets and related equipment. On the other hand, in the design of thermal protection systems for rocket motors or high speed aerodynamic vehicles, the problem of augmented heat transfer rates must be anticipated and provided for.

In many cases, heat transfer considerations govern the design of high performance propulsion systems. With current interest in more energetic chemical fuels and longer thrust durations, the nozzle cooling problem^{4,5,6} is correspondingly intensified. It is for these new propellant combinations that thermochemical effects are likely to become noticeable since a substantial fraction of the reaction products at the chamber pressure and temperature are in the form of light, dissociated gases. Anomalously large transfer rates have already been reported in such systems, and these have been presumed to be due to the effects of exothermic chemical reaction, both in the gas phase and at the gas/solid interface, as well as enhanced radiation from the chemically reacting mixture. However, due to the complexity and expense of full scale rocket motor tests, experimental results are few in number and very often are of limited value for purposes of generalization. A large price has already been paid for the experimental information currently available in the literature.

Taking the view that a more fundamental, though perhaps more academic, set of experimental measurements would prove useful in gaining an understanding of the influence of chemical reaction on heat transfer, this laboratory embarked on such a program in April of 1959 under the support of the United States Air Force.

As a result, two new experimental techniques have emerged which offer comparative.

economy and simplicity and appear to be capable of providing a quantitative understanding of the important thermochemical and radiative energy transport mechanisms. In support of these studies, parallel theoretical investigations have been carried out on catalysis effects in flow systems^{8,9}, and convective heat transfer in dissociated gases and related phenomena^{10,11,12} with application to rocket motor heat transfer. The results of these studies are reported elsewhere¹². The experimental work carried out thus far is described below.

Because of the dominant influence of density level on the rate of chemical reactions in the gas phase, it was decided at the outset to carry out experiments over a wide range of pressures. The difficulties of operating steady flow combustion devices of reasonable size at pressures in the range of 1000 psia suggested the use of a constant volume transient explosion method for the high pressure studies. However, at the lower end of the pressure scale, the steady flow, flat flame subatmospheric burner showed great promise. Thus, the experimental program was divided into two distinct phases which we will arbitrarily designate hereafter as "superatmospheric" and "subatmospheric". In the superatmospheric program we set out to develop an explosion technique for studying transient energy transport rates in reacting gases up to pressures of about 1000 psia. In the subatmospheric program we set out to develop techniques for studying the steady state heat transfer rate to cooled probes immersed in the flame gases at pressures as low as the mm Hg range (between 10^{-3} and 10^{-2} atm). Both phases are described below, and some of the experimental results obtained to date are given. It is felt that the techniques described herein have yet to bear the larger portion of the fruits of which they are capable. This research is a portion of a continuing program at AeroChem devoted to the subject of energy transfer in the presence of thermochemical change.

II. MEASUREMENT OF HEAT TRANSFER TO SOLIDS IMMERSED IN FLAME GASES AT SUBATMOSPHERIC PRESSURES

1. Nature of Problem

The work of Kilham¹³, 14, 15 on radiation cooled circular cylinders in cross flow 13,14 indicated that anomalous heat transfer effects are encountered near the reaction zone of flames burning at atmospheric pressure. In hydrogen-oxygen flames stabilized on a Bunsen type burner, for example, he found that heat transfer rates in or just above the inner cone were higher than computed values based on "conventional" convection correlations. More recently, Cookson¹⁶ and Kilham have corroborated these preliminary findings in a more detailed study of heat transfer from flat lean hydrogenair flames to a stagnation-point heat-flow meter; also at atmospheric pressure. From this work, as well as past experience with the immersion pyrometry of flame gases in regions of active chemical reaction 17, it appears that this enhancement in heat transfer rate is associated in some way with the presence of energetic molecular fragments (free radicals) in the gases wetting the heat transfer surfaces. Since temperature and heat flux measurements are often found to be sensitive to the nature of the surface used (e.g., whether it is a bare metal or coated with quartz), the postulated mechanism of diffusion and surface catalyzed chemical reassociation is quite plausible; although the effects of gas phase chemical reaction within the diffusion boundary layer cannot be ruled out, particularly at atmospheric pressure.

If one now considers low pressure flames, and in particular low pressure flat flames, then the space coordinates of the combustion process are considerably expanded -- reaction zone thicknesses are measured in centimeters rather than microns^{18,19}. Thus, while the dimensions of any heat transfer probe are apt to be large compared to the reaction zone thickness at one atmosphere, in a subatmospheric flame one has the possibility of truly probing the reaction zone. This is advantageous in the present case since there is now ample reason to believe that free radical concentrations show maxima within the reaction zone²⁰. Moreover, these maxima are far in excess of the equilibrium free radical concentration corresponding to complete, adiabatic combustion²¹. For simple free radicals, the dominant gas phase removal processes are termolecular. Thus, one has the further advantage that the nonequilibrium free radical concentrations should persist further downstream of the primary reaction zone at the lower pressures. A closely related phenomenon is the reassociation of free radicals in the vicinity of the probe interface. Since surface catalysis effects will only be observed under conditions of long radical lifetime compared to the

residence time within the diffusion boundary layer, there are <u>a priori</u> reasons to believe that heat transfer specificity effects with various heat transfer surfaces will become more and more marked as the pressure level is reduced. This trend has already been reported by Cutting, Fay, Hogan and Moffatt²² in a series of shock-tube experiments with stoichiometric oxy-hydrogen mixtures.

The previous considerations suggested the construction of a low pressure flat flame burner and a steady state heat transfer probe which would enable the mechanism of energy transport to be studied at various points within the flame. Except for minor departures, the burner design was patterned after similar burners which have been previously operated at this laboratory in connection with the study of ion production in flames²³. However, the heat transfer probe had several novel aspects, most of which are described in the following section. In addition to heat flux measurements, some work has been done on gas temperature measurements using both a sodium line reversal technique, and a compensated hot wire method^{24,25}. As yet, neither of these measurements has been made on a routine basis, and more complete results of this work must of necessity await a future communication. Clearly, if heat flux measurements are ultimately to be interpreted in terms of energy transport mechanisms, determination of the heat transport coefficient will be necessary. For this purpose measurements of flame gas temperature and mass velocity will be a necessary (but not sufficient) adjunct to the heat flux data. Also necessary, but more distant, would be an independent determination of the free radical concentration distribution in the particular flames under study.

2. Heat Transfer Probe

A right circular cylinder oriented transverse to the flow of flame gases can form the basis of a simple calorimetric-type²⁶ heat flux probe, as shown in Fig. 1. In this design, the temperature rise T_2 - T_1 experienced by a known flow rate of coolant passed through the tube is sufficient to determine the average heat flux, provided that edge effects in the flame are avoided and axial heat conduction within the probe is rendered negligible. The edge effects can be minimized by sensing only the temperature rise over a length L of tube which is well imbedded within the flame (i.e., L is considerably smaller than the burner diameter). If axial conduction losses were significant, the effects could always be experimentally eliminated from the data by observing the temperature rise data over a range of coolant mass flows, thereby enabling extrapolation to vanishing temperature rise. In practice, if the Peclet number UL/a based one average coolant velocity U, length L, and coolant thermal diffusivity a is

sufficiently large, convective energy transport will dominate, and axial conduction at the thermocouple locations can be neglected without serious error.

A further design consideration has to do with how representative of the coolant bulk temperature are the measurements T_1 and T_2 . Under conditions of high heat flux from the flame gases to the coolant, the radial temperature differences in the coolant can become comparable to or exceed the desired axial temperature rise, depending on the choice of coolant. Calculations showed that this was certainly true for gaseous coolants and was likely to be true for ordinary liquids, such as water. This means that a small error in the in the axial alignment of the thermocouples can cause a large systematic error in the calculated heat flux. Furthermore, the more non-uniform are the radial temperature profiles at stations 1 and 2, the less likely are the centerline temperature difference measurements to be indicative of the axial rise in mean "mixed" temperature. For these reasons, it was decided to operate the probe with a liquid metal coolant, and mercury proved to be a convenient choice. With this choice, under operating conditions, the radial temperature differences are small compared to the axial temperature rise and, furthermore, a reasonably accurate estimate of the outer surface temperature of the heat transfer probe becomes possible from a knowledge of the observed heat flux and an estimate of the internal (liquid metal side) heat transfer coefficient.

The overall configuration of the heat transfer probe is shown schematically (plan view) in Fig. 2. Liquid mercury enters the probe from a constant head flow system (to be described) and is directed through tubing into a crescent shaped header straddling the burner. The mercury then flows through the thin walled tubing comprising the heat transfer surface and leaves through the elbow at the other end of the crescent shaped header. Type 304 stainless steel was used for all parts wetted by the liquid mercury. The heat transfer tube itself was fabricated from .125" O.D., .003" wall thickness seamless tubing supplied by J. Bishop and Company Platinum Works, Malvern, Pennsylvania. Fig. 3 shows a detailed cross-section of the probe thermocouple and coolant flow configuration. The thermocouples used were of .040" O.D. stainless steel sheathed iron-constantan and were supplied by Aero Research Company, Chicago 7, Illinois. A helix of stainless steel wire was used to maintain co-axial alignment between the thermocouples and the heat transfer tube itself. The packings shown in black are of neoprene and are either standard O-rings or standard Conax Company (Buffalo, New York) In earlier versions of the probe, 0.125" O.D. sheathed thermocouples had been used with bare junctions. In order to record differential temperature rise, however, these janctions had to be coated (electrically insulated) with an epoxy type

(0)

resin; however, this proved unsatisfactory in that the coating life in the heated mercury was erratic. Replacement with ungrounded .040" sheath enclosed thermocouples eliminated the necessity of this coating process and reduced the "out of service" time of the probe considerably. For most of the work reported here, the burner diameter was 10.1 cm and the length L between thermocouple junctions was 5.08 cm.

(%)

As shown in Fig. 3, heat transfer surfaces could be interchanged by first loosening the appropriate neoprene and packings. This was considered desirable for studying the effects of surface catalysis, since the same basic probe could be used for heat transfer experiments with surfaces of widely different catalytic activity. For this purpose several sections of the thin walled stainless tubing were electroplated with platinum, and several sections were given a coat of silicone (Dow Corning No. 803). Comparative data using both types of surface were then taken in an ethyleneair flame and a hydrogen-oxygen flame in an effort to observe any systematic effects due to preferential free radical recombination on the platinum. With further improvements in the probe technique, we hope to extend the limited amount of data presented herein to other mixture ratios and other surfaces.

The arrangement of the constant head mercury flow system is shown in Fig. 4. Basically, mercury flows from an elevated reservoir (item 2) through the probe to a Sigma-motor "finger pump" (item 4) which continuously replenishes the reservoir. Early flow rate determinations were made using the steady state pressure drop across a restriction (item 5) in the flow; however, this method was abandoned in favor of a simple volumetric "batch" method (item 7) owing to the need for frequent recalibration. With this coolant flow system, extreme care had to be exercised to make sure that small air pockets were not trapped within the probe itself during a run.

To examine experimentally the severity of axial conduction errors, a series of bench tests was run at atmospheric pressure using a shielded Meker burner. Apparent heat flux was plotted against the differential emf E_2 - E_1 over a range of coolant flow rates. In a typical case, more than a two-fold change in coolant temperature rise (56°C to about 122°C) produced no systematic change in apparent heat flux, the latter remaining constant to within $\pm 4\%$. The Peclet numbers for these extremes (based on the length L) were 550 and 726 respectively. In practice, the subatmospheric flame tests were run at mercury flow rates corresponding to E_2 - E_1 \approx 1 mv or about 20°C temperature difference. The probe data recorded included:

We are indebted to the Chemical Division of Engelhard Industries, Newark, N.J., for .this service.

For iron-constantan in the temperature range investigated, the Leeds and Northrup Company thermocouple tables give 1 mv = 18.3° C, to within $\pm 1.5\%$.

1. the emf E_1 ,

2. the differential emf E_2 - E_1 , and

 the time to fill a burette of known volume (usually 50 cc) with mercury.

From these data, the average heat flux \ddot{q} " was computed from the steady state energy balance relation

$$\bar{\mathbf{q}}'' = \frac{\dot{\mathbf{m}}_{Hg} \, \bar{\mathbf{c}}_{p,Hg} \, (\Delta T)_{Hg}}{\pi \, d \, L} \tag{1}$$

where

6

 $\bar{c}_{p,Hg}$ = average specific heat of mercury [(cal)(gm)⁻¹(o C)⁻¹] over the temperature interval ΔT

 $(\Delta T)_{Hq}$ = axial temperature rise of mercury ($^{\circ}$ C)

d = outer diameter of heat transfer surface (cm)

L = axial distance between thermocouple junctions (cm)

For this purpose the thermal and physical data assembled in Appendix 1 were used.

3. Subatmospheric Burner

The burner assembly used in the present work, shown in Fig. 5, is basica by similar to those used for earlier flame studies at this laboratory²³. The burner itself is a thin walled, 10 cm diameter brass cylinder mounted on a 2.54 cm steel support and supply tube. Within the brass cylinder are a series of five stainless steel screens separated by spacers for uniformization of the flow of pre-mixed gases. The burner can be moved vertically by means of a threaded section of the support tube and suitable gearing. The burner support conduit comes through a Teflon packing gland in the vacuum jacket. Since the burner can be raised and lowered while in operation, one thereby obtains a traverse using probes which are fixed with respect to the burner housing. The subatmospheric pressure is maintained by the action of a Stokes mechanical vacuum pump of nominal pumping capacity 360 cfm. Four large openings, at right angles to one another, are provided in the housing for visibility and instrumentation lead-throughs. The housing itself was fabricated from stainless sheet steel and provided with four slip flanges and two weld-on flanges. The position of the probe (mounted by means of one of the slip flanges) with respect to the burner screen was

determined from the reading of a digital counter linked to the gear system (1 count = 4.55×10^{-3} cm).

Gas flows are metered by individual rotameters (variable area flow meters) together with a total gas flow rotameter. The mixture ratio is computed from the readings of the individual rotameters; however, the total flow is not the sum of the individual flows because of the presence of a bleed check valve introduced between the total and individual flow meters. By exhausting varying quantities of the mixture to the atmosphere, the check valve enables the combustible gas composition to be maintained nearly constant while varying either the total flow rate or pressure. Thus, any particular flame can be ignited at a convenient pressure, and the pressure level can then be reduced while maintaining the mixture composition substantially constant.

Ignition is accomplished by passing a spark between an electrode and the pilot rim in the presence of a small amount of pilot gas, the latter being introduced through a separate tube of small bore. The resulting diffusion flame at the burner rim then ignites the main pre-mixed gas flow.

4. Experimental Results

To check out the burner-heat flux probe system as a whole, the first series of low pressure experiments was done with ethylene-air flames over a range of pressure and mixture ratio. A particular flame was then singled out in order to study the repeatability of the measurements; this was a lean ethylene-air flame ($\Phi = 0.838$) at a nominal pressure level of 14 mm Hg. Fig. 6 shows the heat flux distributions measured with both silicone coated and platinized probes on four different days. It is observed that:

- a. peak heat fluxes for both the platinized and silicone coated probes are nearly the same. The platinized probe peak heat flux is slightly larger (about 5%) and tends to occur somewhat upstream of that for the silicone coated probe, but neither of these effects is particularly definitive;
- b. peak heat fluxes for both probes occurred noticeably down-stream of the region of visible luminousity. In the case of the platinized tube, the distance downstream amounted to about 0.7 visible flame thicknesses (measured from rear of zone). These visible flame zone thicknesses were about 2.5 times the probe diameter (d = 0.318 cm);

- c. peak heat fluxes were about 0.75 (cal)(cm)⁻²(sec)⁻¹ at this pressure level. The heat fluxes decreased with distance in the burned gases at about the same rate for both probe surfaces. The major portion of this decrease is attributed to radial heat loss, perhaps augmented by recirculation flows within the burner housing downstream of the luminous zone;
- d. for any given run, experimental heat fluxes at a prescribed distance from the burner could be reproduced to within about ±3%. On different days, however, the reproducibility is of the order of only ±15% in the regions of small (rapidly rising) heat flux, upstream of and within the luminous zone. The major cause of this loss in precision is felt to be variation in the position of the flame with respect to the burner rim. This will be discussed further in connection with related experiments in the hydrogen/oxygen system.

Since free radical concentrations in hydrocarbon-air flames are believed to be quite small²⁷, the ethylene-air results summarized above are not unexpected. Because of the complexity of the gas mixture enveloping the probe surfaces (composed of CO, CO₂, O₂, N₂, H₂O and smaller amounts of OH and O), theoretical interpretation of the ethylene-air flame results is difficult. For these and other reasons, the experimental effort was redirected to the hydrogen-oxygen flames, in which there is, at present, considerable theoretical, as well as practical, interest.

• In the case of the hydrogen-oxygen flame, the primary reaction zone is not visible. Furthermore, as suggested by the ethylene-air flame data discussed above, the distance from the probe to the burner screen is not a satisfactory measure of the probe location within the flame zone since the flame "stand off distance" may vary from day to day. One thus requires a position measurement relative to the reaction zone itself. Two general methods come to mind, viz. an immersion method, such as the use of an auxiliary thermocouple fixed with respect to the probe, or an external radiation detector fixed with respect to the probe. Even if the reaction zone were visible, the human eye is inadequate for accurately determining the flame position. For the hydrogen-oxygen flame, the human eye is out of the question. It was therefore

It will probably be desirable to control the burner rim temperature, as well, in future experiments.

decided to employ a large diameter radiation cooled Pt/Pt-13% Rh thermocouple wire (ceramic coated to a nominal diameter of 2.5 mm) stretched parallel to the probe surface with the junction located at the mid point. By shifting the observed heat flux data in the streamwise direction until the "temperature" profiles obtained with the thermocouple were aligned, the relative output of the thermocouple could then be used to ascertain the probe position within the flame zone. This procedure has the advantage that both the heat flux and "temperature" can be recorded simultaneously with no particular difficulty.

(1)

Fig. 7 shows a typical pair of such profiles obtained with a platinized probe in a rich ($\delta = 1.43$) oxy-hydrogen flame at 5 mm Hg pressure. A striking feature evident here, as in all of the 5 mm Hg oxy-hydrogen data thus far examined, is the rapid spatial decay of heat flux in the downstream portions of the flame; i.e., the heat flux decays at a rate comparable to the rate of increase in the upstream regions of the flame. Also of interest is the fact that the point of maximum apparent temperature occurs noticeably downstream of the point of peak heat flux. This was also observed for silicone coated surfaces in the same flame, and is suggestive of energy transfer mechanisms other than ordinary heat convection within the reaction zone. A total of 6 traverses were made in this flame (3 using platinum probe surfaces, 3 using silicone coated surfaces) in the hope of being able to study the differences between the heat flux to each of these surfaces as a function of position. Surprisingly enough (in the light of the ethylene-air data) the repeatability proved so poor that definitive conclusions could not be drawn. Thus, while the maximum observed value of the peak heat flux with a platinum coated probe exceeded the maximum value of the peak heat flux with a silicone coated surface by as much as 17 percent, the minimum recorded peak heat flux with a platinum probe was less than the minimum recorded silicone coated probe peak heat flux by about this same amount. As of the moment, the cause of this lack of repeatability in the oxy-hydrogen system can only be speculated upon (see part II-5). Future research will therefore be directed at this most immediate obstacle to the elucidation of gas/solid energy transfer mechanisms in chemically reacting mixtures at subatmospheric pressures.

using Astroceram "A" high-temperature cement (American Thermocatalytic Corp., New York, manufacturers)

particularly in the case of the platinum probe data, where the peak heat fluxes on 3 different days varied by as much as about +15%. The value shown in Fig. 7 was the lowest in absolute value.

5. Summary of Subatmospheric Phase

A novel method of measuring steady-state heat fluxes to strongly cooled catalytic and non-catalytic solids within subatmospheric flames (in the mm Hg range) has been described and used to obtain preliminary heat flux data as a function of position in flat ethylene/air and hydrogen/oxygen flames stabilized on a 4 inch diameter burner. The present probe lends itself to further miniaturization, (The Bishop Company supplies thin walled stainless tubing smaller by a factor of two than that used here) and can be operated for long periods of time over a wide range of total pressures.

In the case of a lean (Φ = .84) ethylene/air flame at 14 mm Hg total pressure peak heat fluxes to both platinized and silicone coated probe surfaces occurred noticeably downstream of the region of visible luminousity. However, no appreciable difference in peak heat flux to the different surfaces was observed for this hydrocarbon/air flame. Similar measurements in a rich oxy-hydrogen flame at 5 mm total pressure suggest that the region of peak heat flux to both platinized silicone coated probe surfaces occurs upstream of the region of maximum gas temperature. Here, however, the precision of the data was not adequate to quantitatively study the dependence of the difference in heat fluxes as a function of position. The wide scatter of the data for the platinum coated probe suggests that the reproducibility of the platinum surface itself may have to be controlled more carefully than was done here. Future research would be directed at this obstacle and have among its foremost goals the acquisition of data on the dependence of the difference in heat flux on both position and total pressure within chemically reacting hydrogen-oxygen mixtures.

Platinized probe surfaces were degreased with trichloroethylene prior to each run.

III. TRANSIENT HEAT TRANSFER RATES FROM THE HIGH PRESSURE AND TEMPERATURE PRODUCTS OF HYDROGEN-OXYGEN EXPLOSIONS IN A VESSEL OF CONSTANT VOLUME

1. Introduction

Since the experimental complexity, and therefore the cost of actual liquid propellant rocket motor heat transfer tests, is so large one is led to inquire whether something can be learned about the energy transfer mechanisms involved without having to operate actual rocket motors at pressures up to 1000 psia. Preferably, the experimental method sought should have the attributes of low cost and simplicity; i.e., it should enable rapid testing in the laboratory and utilize small amounts of propellant without the need for extensive facilities or equipment. A similar question has recently been answered in the affirmative by Griffin, Turner and Angeloff²⁸ with regard to the determination of the specific impulse of new propellants. These investigators have shown that constant volume combustion in a ballistic bomb can provide accurate data from which the specific impulse can be obtained. We propose here to show that certain important molecular transport coefficients (viz. the thermal diffusivity and radiative emissivity) can be profitably investigated in a constant volume bomb. This type of information would not only comprise a useful supplement to experimental data obtained in flow systems using the same propellants but also could be incorporated into a more comprehensive theoretical analysis of energy transfer processes in chemical reactors in general (and rocket thrust chambers in particular).

In what follows, we will discuss certain theoretical and experimental aspects of the use of constant volume explosions to study energy transport in chemically reacting systems.

2. Theory

Explosions of premixed gases in closed vessels have been studied for many years^{29,30}; however, the emphasis has been upon the reaction time and relation between the peak pressure and the thermodynamic properties of the reactants and products. The recent work of Medvedev³¹ (1958) has once again made it clear that spherical bomb explosion studies can yield very useful results pertaining to the equilibrium thermodynamic properties of gases at high temperatures and pressures. It appears to the writer that the potentialities of this technique for determining transport properties of high temperature and pressure gases remain largely unexploited.

The essentials of the explosion method can be described as follows. A premixed combustible gas mixture is admitted into a pressure vessel cavity and ignited at the center of this "bomb" by either a spark or an electrically heated wire. The chemical energy release following the ignition process causes the pressure in the vessel to rise rapidly to some peak value \boldsymbol{p}_{m} in a time \boldsymbol{t}_{m} at which the reactants may be said to be consumed. At this point the hot explosion products, which are now in contact with the cooler walls of the bomb, begin to lose appreciable quantities of heat, principally by conduction and radiation. Since the internal energy of the enclosed gases is related to the pressure, the cooling period is accompanied by a gradual pressure decay (see Fig. 8) which is easily measured. Many good records of this type may be found in the literature and, as will be seen, can be interpreted from the point of view of energy transfer in reacting systems. Unfortunately, however, some of the best records have been obtained in cylindrical bombs of small aspect ratio with noncentral ignition. In the past, more interest has been displayed in the pressure rise portion of the record than in the detailed behavior of the "cooling curves". For the present purpose, this emphasis will be reversed.

a. Relation Between Average Heat Transfer Rate and Rate of Pressure Decay. To appreciate the relation between the pressure history and the amount of heat loss, consider a mass of gas of volume V with local internal energy per unit mass e and local density o. Then at any instant t of time, the energy content of the gas within the vessel will be

$$E(t) = \int \rho e \ dV \tag{2}$$

If the specific internal energy e is considered to be a function of ρ and T alone, then the time rate of change of E can be written

$$\frac{dE}{dt} = \int \rho \left[\left(\frac{\partial e}{\partial T} \right)_{\rho} \frac{\partial T}{\partial t} + \left[\left(\frac{\partial e}{\partial \rho} \right)_{T} + \frac{e}{\rho} \right] \frac{\partial \rho}{\partial t} \right] dV$$
 (3)

Since the pressure will be nearly uniform throughout the volume, the perfect gas law implies that

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{1}{V} \int \frac{\partial}{\partial t} \left[\frac{\rho R_{\mathrm{u}}^{\mathrm{T}}}{\pi_{\mathrm{u}}} \right] \mathrm{d}V \tag{4}$$

Expanding the integrand, it is observed that, under the following conditions

$$\mathfrak{m} \stackrel{\sim}{=} \text{constant} = \overline{\mathfrak{m}}$$
 (5a)

$$(\frac{\partial e}{\partial T})_{\rho} \approx constant = (\frac{\overline{\partial e}}{\partial T})_{\rho}$$
 (5b)

$$e = T(\frac{\partial e}{\partial T})_{\Omega} - \rho(\frac{\partial e}{\partial \rho})_{T}$$
 (5c)

dE/dt and dp/dt will be linearly related by the simple law

$$\frac{dE}{dt} = V(\frac{\overline{\partial e}}{\partial T})_{O}(\frac{\overline{m}}{R}) \frac{dp}{dt}$$
 (6)

even when the internal energy e and hence the temperature T vary from point to point within the vessel. The average heat transfer rate \dot{q} " per unit area is then given by (1/S)(dE/dt) or

$$\bar{q}''(t) = \frac{V}{S} \left(\frac{\overline{\partial e}}{\partial T} \right)_{\rho} \left(\frac{\overline{m}}{R} \right) \frac{dp}{dt}$$
(7)

where, for a sphere, V/S = R/3. The total heat removed up to time t (measured from the moment of peak pressure) is:

$$Q(t) = S \int_{0}^{t} \overline{q}''(t) dt \approx V(\frac{\partial e}{\partial T})_{\rho} (\frac{\overline{n}}{R_{U}}) [p_{m} - p(t)]$$
 (8)

and, in particular, $Q(\infty)$ will be given by Eq.(8) when p(t) is evaluated at $t=\infty^{\ddagger}$.

for a perfect gas e = e(T) so that $(\frac{\partial e}{\partial \rho})_T \equiv 0$. Condition (5c) is then satisfied for a perfect gas with constant c_v (specific heat), if e(o) = 0.

When water vapor condensation occurs, the observed pressure $p(\infty)$ must be corrected upwards to give the pressure that would have existed had no condensation taken place. The influence of condensation is discussed further in Appendix 2.

Thus

$$Q^* \equiv \frac{Q(t)}{Q(\infty)} \simeq \frac{p_m - p(t)}{p_m - p(\infty)} = \frac{\Delta p(t)}{\Delta p(\infty)}$$
(9)

b. <u>Graphical Determination of Relative Heat Loss Q* Using Thermodynamic Charts (Energy-Density Diagram)</u>. An alternative procedure for determining $Q^*(t)$ seems more reasonable when applied to gas mixtures for which the conditions (5a)(5b)(5c) are not closely satisfied. Thus, instead of taking $Q(t) \sim \Delta p(t)$, recourse will be made to a graphical representation of the caloric equation of state e(p;p) of the products of reaction. It is recalled that the explosion process itself, as well as the subsequent cooling process, takes place in a constant volume with no loss of mass through the vessel walls. Therefore, if the actual non-uniform gas mixture which exists at each time t is replaced by a fictitious uniform gas in thermochemical equilibrium at the same pressure and density, the cooling process for this fictitious gas may be considered to be represented by a vertical line (line of constant density) on the e-p (see Fig. 9) plane. Then by matching the observed pressures with the corresponding isobars, one can plot the normalized heat loss

$$Q^* = \frac{\Delta e(t)}{\Delta e(\infty)} \tag{10}$$

where $\Delta e(\infty)$ can be evaluated from the experimental pressures p_m and $p(\infty)$ or obtained from an <u>a priori</u> knowledge of the final gas temperature.

An accurate internal energy-density diagram for the equilibrium products of stoichiometric hydrogen-oxygen explosions is shown in Fig. 10. This chart was constructed using an IBM 650 to obtain numerical solutions to the equations of mass action and overall stoichiometry. All input thermochemical data and reference energies are those of Ref. 32.

c. Relation Between Relative Heat Loss Q^* and Molecular Transport Properties of the Constituent Gases. Since the relative heat loss Q^* is not an end in itself, we must inquire further as to the relation between Q^* (t) and the energy transport properties of the confined high temperature-high pressure gases.

6 0

If the heat capacity of the bomb is sufficiently large, the final gas temperature (at $t=\infty$) will be very nearly T_0 , the initial bomb wall temperature.

To illustrate one method by which this problem might be approached, consider for the moment that all of the heat loss occurs by conduction to the cold walls and imagine that the sphere of hot gas existing at the moment of peak pressure behaves like a solid sphere of constant thermal diffusivity α , "quenched" by sudden contact with cold walls at radius R. Then Q would increase with time in accord with the well known solution 33 to the Fourier transient heat conduction equation

$$Q^{*}(\tau) = 1 - \frac{6}{\pi^{2}} \sum_{n=1}^{\infty} \frac{1}{n^{2}} \exp(-n^{2} \pi^{2} \tau)$$
 (11)

where

 $\tau = \alpha t/R^2 = nondimensional time$

 $Q^*(\tau)$ = normalized integrated heat loss

 α = thermal diffusivity

R = radius of spherical bomb

Values of this function are given in Table I and plotted in Fig. 11. Observe that for small values of τ we have the asymptotic behavior

$$Q^*(\tau) \sim \frac{6}{\sqrt{\pi}} \cdot \sqrt{\tau} \tag{12}$$

If data were available at sufficiently small values of τ this result could be used to obtain experimental values of the effective diffusivity α by plotting $(\pi/36)$ $(Q^{\#})^2$ as a function of t/R^2 and measuring the slope of the best straight line through the data.

To illustrate this procedure, let us re-examine the conductive heat loss data reported by David³⁴ (1920) for a 15% coal gas-air explosion in a short cylinder with d = 30 cm and L/d = 1.

In constructing Table II, we have corrected David's data for heat losses before the time of peak pressure (i.e., 0.05 sec) by subtracting from the apparent value of Q^* the value of Q^* at $t=t_m$. Fig. 12 shows a plot of $\frac{\pi}{36}(Q^*)^2$ against t/R^2 . The inferred thermal diffusivity in this case is about 4.8 cm²/sec.

 $^{^{\}dagger}$ Radiation loss will be discussed in a subsequent section.

TABLE I

TRANSIENT DIFFUSION IN A SOLID SPHERE 33

τ	1 - Q*	Q [#]	√ 1
0.000	1.000 0.896	0.000 0.104	0.00000
0.002	0.855	0.145	0.04472
	0.824	0.176	0.05477
0.004	0.798	0.202	0.06325
	0.776	0.224	0.07071
0.006	0.756	0.244	0.07746
	0.739	0.261	0.09367
0.008	0.721	0.279	0.08944
	0.706	0.294	0.09487
0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09	0.691 0.581 0.504 0.443 0.393 0.351 0.314 0.283 0.254	0.309 0.419 0.496 0.557 0.607 0.649 0.686 0.717	0.1000 0.1414 0.1732 0.2000 0.2236 0.2449 0.2646 0.2828 0.3000
0.10	0.230	0.770	0.3162
0.15	0.139	0.861	0.3873
0.20	0.084	0.916	0.4472
0.25	0.052	0.948	0.5000

TABLE II

FRACTIONAL HEAT LOSS BY CONDUCTION; [DAVID³⁴ (1920)]

15% Coal Gas-Air in 30 cm L/d = 1 Cylinder

t - t _o (sec)	Q _a *	t - t _m (sec)	Q _a *051
0.05	0.051	0.00	0.000
0.10	0.144	0.05	0.093
0.15	0.203	0.10	0.152
0.20	0.245	0.15	0.194
0.25	0.277	0.20	0.226
0.30	0.300	0.25	0.249
0.40	0.344	0.35	0.293
0.50	0.376	0.45	0.325

Now, in practice, the attainable accuracy of a method of this type appears to be limited by four considerations:

- the pressure and temperature dependence of the thermal diffusivity of gases,
- 2. the compressibility of the gas mixture within the fixed enclosure,
- 3. possible enhancement of energy transfer due to gravity induced natural convection currents within the vessel, and
- 4. energy loss by other mechanisms (e.g., radiation)

The first two of these factors will be briefly discussed in the remainder of this section. The remaining factors will be dealt with in separate sections.

Since the thermal diffusivity α of a gas depends almost linearly upon the inverse of the pressure level, the previous procedure can only be useful when $\Delta p/p_m$ is small; <u>i.e.</u>, in effect the diffusivity of the medium increases during the experiment. Thus, the method outlined above would inherently give the diffusivity at the pressure p_m only by extrapolation to zero time $(\tau \to 0)$. This is not a serious limitation in itself since p_m can be varied at will by varying the initial pressure (before explosion).

Because the thermal diffusivity is also temperature dependent, a method of data reduction of the type described earlier also yields an "effective" constant

property diffusivity which after extrapolation to zero time is some average between $\alpha(p_m,T_m)$ and $\alpha(p_m,T_w)$. If the functional form of the temperature dependence of α were known, then solutions to the transient heat conduction equation for variable diffusivity could be coupled with the experimental data to yield $\alpha(p_m, T_m)$. For instance, Hansen's one dimensional solutions^{35,36} to the heat conduction equation could be carried over to the case of spherical symmetry with no difficulty. An interesting question which arises when this is done, however, has to do with effects of thermally induced volume changes on the behavior of a completely enclosed compressible gas. Qualitatively speaking, when the exterior regions of gas are suddenly cooled, a contraction occurs which must be compensated for by a radial expansion of the central regions of hotter gases. The result of this expansion process is to increase the temperature gradient at the wall, and hence increase the rate of heat loss at each time t. To the writer's knowledge, the only treatment of this problem is the linearized treatment of Rayleigh 37 (1899). Rayleigh clearly stated that, even in the limit of infinitesimal distrubances: "When one part of the gas expands in consequence of the reception of heat by radiation or conduction, it compresses the remaining parts and these in their turn become heated in accordance with the law of gases. To take into account this effect, a special investigation is necessary". His solution to the linearized problem gives Q^* as a function of a new nondimensional time τ' related to τ by the factor π^2/γ , where $\gamma \equiv c_p/c_v = 1.41^{\dagger}$. When $\gamma = 1$, the solution to Rayleigh's problem reduces to the Fourier solution for a spherical solid. It is observed that the use of the Fourier solution [Eq.(11)] when in fact $\gamma = 1.41$ causes the inferred thermal diffusivity to be systematically overestimated by about 40%. This points up the need for more realistic solutions to the transient (nonlinear) heat conduction problem than are currently available in the literature. As is apparent, the accuracy of the property value inference depends upon the accuracy of the available solutions. Both the Fourier and Rayleigh solutions are strictly applicable to the case of constant thermal diffusivity. It can be verified from the foregoing analysis of David's data, however, that most of the available points fall in a region of time which not only exceeds the range of validity of the asymptotic relation (12) but also exceeds

Unfortunately, Rayleigh's solution does <u>not</u> have the self-similarity*property suggested by the inclusion of γ in the time variable. The values of Q versus τ given in Table III are thus valid only for $\gamma=1.41$ and cannot be obtained from Fig. 11 by merely re-interpreting the independent variable.

TABLE III

RAYLEIGH'S SOLUTION³⁷ (1899): *TRANSIENT HEAT CONDUCTION IN A

SPHERICAL MASS OF AIR ($\Upsilon = 1.41$) CONFINED BY WALLS AT CONSTANT TEMPERATURE

τ'	1 - Q*	Q*	$\tau = \frac{\Upsilon}{\pi^2} \cdot \tau'$	√τ
	1.000	0.000		2 00000
0.000	1.000	0.0000	0.000000	0.00000
0.05	0.7037	0.2963	0.007143	0.08452
0.10	0.6037	0.3963	0.01429	0.1195
0.184'	0.5000	0.5000	0.0263	0.162
0.20	0.4811	0.5189	0.02857	0.1690
0.30	0.4002	0.5998	0.04286	0.2070
0.40	0.3401	0.6599	0.05715	0.2391
0.50	0.2926	0.7074	0.07143	0.2673
0.60	0.2538	0.7462	0.08572	0.2928
0.70	0.2215	0.7785	0,1000	0.3162
0.80	0.1940	0.8060	0,1143	0.3381
0.90	0.1705	0.8295	0.1286	0.3586
1.00	0.1502	0.8498	0.1429	0.3780
1.50	0.0809	0.9191	0.2143	0.4629
2.00	0.0441	0.9559	0.2857	0.5345
		•		

t by interpolation

the range of values in which near constancy of the thermal diffusivity is a good approximation. Since the thermal diffusivity α appears in these transient conduction solutions as a multiplier of the time variable t, the effect of variations in α is to "stretch" the time scale of the process. Using this notion, the full Rayleigh solution can be utilized to obtain the diffusivity α_{m} as follows.

Let us assume that the effective thermal diffusivity is a function only of the pressure, p, (which is nearly uniform throughout the vessel at any time) and of some average ("film") temperature T_f . Since both p=p(t) and $T_f=T_f(t)$, the average diffusivity can be regarded as some function of time. This being the case, inspection of the transient heat conduction equation reveals that the constant property solution will apply to this situation by merely re-interpreting the variable τ as

$$\tau = \frac{1}{R^2} \int_0^t \alpha(t) dt$$
 (13)

For example, as a reasonable first approximation, consider the "hard-sphere" kinetic theory dependence

$$\alpha \sim T_f^{3/2} p^{-1}$$
 (14)

Let us further assume that the "film" temperature T_f is not very different from the arithmetic mean of the average gas temperature \overline{T} in the vessel (as determined from the pressure) and the wall temperature T_w (nearly constant), <u>i.e.</u>

$$T_{f} \stackrel{\sim}{=} \frac{1}{2} (\overline{T} + T_{w}) \tag{15}$$

In the integrand of Eq.(13) we then have

$$\alpha(t) = \alpha_{\rm m} \cdot (T_{\rm f}/T_{\rm m})^{3/2} (p_{\rm m}/p)$$
 (16)

where $T_f(t)$ is given by Eq.(15). If we define a new "stretched" time t_{λ} by

$$t_{\lambda} \equiv (\frac{1}{2})^{3/2} \int_{0}^{t} \left[(p/p_{m}) + (T_{w}/T_{m}) \right]^{3/2} (p/p_{m})^{-1} dt$$
 (17)

then $\tau=(\alpha_m/R^2)t_\lambda$. Since the integrand of Eq.(17) is known if the pressure record p(t) is known, the calculation of $t_\lambda(t)$ presents no difficulty. The determination of α_m then proceeds as follows. From a knowledge of the relative conductive heat loss up to time t, the corresponding value of τ is obtained from the Rayleigh solution. Values of τ obtained in this manner could then be plotted against t_λ/R^2 . If the postulated heat loss mechanism is correct, a straight line of slope α_m would be obtained.

d. Possible Buoyancy Effects: Transient Natural Convection. Another important question in the use of the constant volume explosion technique is: How much time is available before natural convection effects would significantly disturb heat transfer processes occurring within the vessel? This question is difficult to answer a priori, and only a limited amount of available explosion data bear upon it. No useful generalizations have appeared in which the role of the important parameters have been displayed.

Lewis and Von Elbe^{38,39} have observed that under certain conditions a break appears in the later history of the cooling curve at which point the heat transfer rate to the vessel walls is suddenly increased. This break is most noticeable if the

explosion products have a large thermal conductivity and low density; substitution of heavy diluent gases (e.g., argon) for light diluents (e.g., helium) makes the effect more gradual. Lewis and Von Elbe interpret this phenomenon as constituting further evidence that a radial temperature gradient exists in the gas at the moment of peak pressure. It is the convective rise of this hot core of gas which presumably increase the heat transfer rate. Actually, even if the gas temperature at the moment of peak pressure were uniform, it is possible to account for this phenomenon by merely invoking the temperature non-uniformities brought about by sudden contact with the cold walls. Indeed, it will be seen to be possible to make an estimate of when this convective augmentation should occur, according to this latter model.

In his study of steady state free convection in horizontal concentric cylinders, Kraussold⁴⁰ found that there was a threshhold value of the product

$$Gr \cdot Pr_{\lambda} = (\delta^3 g\beta \Delta T/\nu^2)(\nu/\alpha)$$
 (18)

beyond which the effect of natural convection became noticeable, i.e., no appreciable bouyancy effects were observed until $\text{Gr} \cdot \text{Pr}_{\lambda} > 10^3$. Since no transient data applicable to the sphere is available, the following analogy seems reasonable for order of magnitude purposes.

Imagine the transient sphere problem to be equivalent to a series of steady state concentric sphere experiments with slowly increasing clearance. Physically, the clearance over which the large temperature change occurs becomes the thickness of the thermal layer which propagates into the hot gas. At the time the Grashof number-Prandtl number product based on this clearance exceeds about 10³, we should therefore expect to begin to see the effects of gravity-induced convective currents within the vessel.

In this way, the steady state experiments of Kraussold can be used to obtain a quasi-steady estimate (which is probably conservative) of the duration of the purely conductive portion of the cooling curve.

• If we let τ_{crit} be the critical value of τ beyond which bouyancy effects become observable, then the argument above leads to the following law

$$\tau_{\text{crit}} \stackrel{\sim}{=} 6.2 (G_{\text{r}} \cdot P_{\text{r}_{\lambda}})^{-2/3}$$
 (19)

where Gr is now based on the bomb radius R. In dimensional form, the time t crit should then be independent of bomb size, being proportional to

$$t_{crit} \propto v^{2/3} a^{-1/3} (g\beta\Delta T)^{-2/3}$$
 (20)

or, equivalently

$$t_{crit} \propto (Pr_{\lambda})^{2/3} \alpha^{1/3} (g\beta\Delta T)^{-2/3}$$
 (21)

This last form can be used to estimate an approximate peak pressure dependence, i.e.,

$$t_{crit} \propto p_{m}^{-1/3} \tag{22}$$

Thus, the shortest useful test times should occur at the highest peak pressures. According to this model, Lewis and Von Elbe's criterion when the effect is most "marked" correspond to those cases for which we would expect t_{crit} to be <u>large</u>. When the effect is not "marked", it is probably occurring everywhere since t_{crit} is smaller under these conditions of conductivity and density.

For a six inch diameter bomb giving a peak pressure of 1000 psia in the oxyhydrogen system, the previous estimate leads to the conclusion that convection effects would not appear before about 10 percent of the energy had been lost to the vessel walls by conduction, and this would take about 20 milliseconds to occur. It should be added that for a stoichiometric hydrogen-oxygen explosion in vessels of this size, the rise time (time from ignition to peak pressure) for initially atmospheric gaseous explosions, is of the order of only 2 milliseconds^{29,30}. For loading pressures (approximately 120 psia) necessary to achieve final pressures of the order of 1000 psia, the rise time should be even less than 2 milliseconds. One is therefore lead to believe that diffusivity experiments of the type investigated here can be done without having to adopt artificial means (e.g., rotation) to suppress or delay buoyancy effects.

While this conclusion is by no means certain, it is probably wisest to proceed upon this assumption and to look for the effects of buoyancy in the longtime pressure-records. Local heat flux measurements obtained with the vessel in different angular positions could also be used to determine the severity of these buoyancy effects.

e. Energy Loss by Radiation to the Bomb Walls. In all gaseous explosions, some fraction of the total chemical energy liberated is radiated to the walls of the containing vessel. In 1907, Hopkinson⁴¹ observed that the peak pressure in coal gas/ air explosions was slightly influenced (3%) and the rate of pressure decay markedly influenced (50%) when the walls of a silver-plated pressure vessel were blackened with lampback. H. T. David42, extending the work of Hopkinson, continuously monitored the radiation escaping through a small Flourite window in the bomb. For the case of a 25.4% hydrogen-air mixture with $T_m = 2400^{\circ}$ K, only 0.5% of the heat of combustion was lost by radiation during the explosion period and 16.1% during the entire course of the explosion. For the case of a 15% coal gas-air mixture, David found that the percentage of the heat of combustion emitted as radiation decreased with increased initial pressure. Recent measurements by Leah and co-workers 43,44 on radiation losses during explosions of dry carbon monoxide-air mixtures (25% CO, 75% air) indicate that at the moment of peak pressure about 12% of the heat of combustion has been lost by radiation; 20% of this loss is chemiluminescent in nature. For times of the order of $(3/2)t_m$, the corresponding values are 17.6% for the total radiation loss of which chemiluminescence is responsible for 14%. The addition of 0.52% hydrogen reduced the total radiation loss up to t_m to only 2.1% of the heat of combustion. Of this, 17.8% is attributed to chemiluminescence. In the case of hydrogen-air explosions, very little chemiluminescence has been observed⁴⁵. It appears then that even when chemiluminescence is important, it is only important when the total radiation flux is small. For high pressure explosions, in which hydrogen is the combustible gas, the energy lost to the walls by radiation up to the moment of peak pressure probably does not exceed 0.5% of the total heat of combustion.

Since radiation can contribute significantly to the relative heat loss $Q^*(t)$, the data reduction procedure outlined earlier for determining the diffusivity a_m will only succeed if the Rayleigh solution is entered not with the <u>total</u> relative heat loss Q^* as determined from $\Delta p(t)/\Delta p(\infty)$ but with the "conductive" portion $Q_{\lambda}^* = Q^* - Q_{\epsilon}^*(t)$ where $Q_{\epsilon}^*(t)$ represents the fractional heat loss due to radiation up to time t. Granting that something is known about the functional form of Q_{ϵ}^* , it is possible that a single explosion experiment (in which only the pressure trace is recorded) could be used to extract not only the thermal diffusivity of the gas mixture at the moment of peak pressure, but also the effective radiative emissivity of this gas.

Consider, for simplicity, that the walls of the enclosure are perfect absorbers. Assume further that with the gas mixture is associated a total hemispheric emissivity $\tilde{\epsilon}$, which is a function only of the optical density of some species k and

the average temperature in the vessel (as determined from the instantaneous pressure). If, over a small range of pressures and temperatures near p_m and T_m , the mole fraction, x_k , of species k does not appreciably change, then the emissivity $\bar{\epsilon}$ can be represented by a power law⁴⁶ of the form

$$\bar{\epsilon} \propto (pR)^a \, \bar{I}^b$$
 (23)

Since the radiation heat loss up to time t can be written

$$Q_{\varepsilon}(t) = 4\pi R^2 \int_{0}^{t} \bar{\varepsilon} \sigma \, \bar{T}^4 \, dt \qquad (24)$$

we then have.

$$Q_{\varepsilon}^{*} = \frac{4\pi R^{2}}{Q(\infty)} \cdot \varepsilon_{m} \sigma \, \bar{T}_{m}^{4} \int_{0}^{t} (p/p_{m})^{4+a+b} \, dt$$
 (25)

The sum, a+b, appearing in the exponent of p/p_m is usually a small fraction of 4 and can sometimes be estimated in advance from a knowledge of the principle radiating species. When this is the case the integral appearing in Eq.(25) defines a new "stretched" time t_E which is immediately calculable from the experimental pressure-time trace. Then Q_E will be linearly proportional to the product of t_E and the as yet undetermined parameter ϵ_m . Since each of the remaining factors is calculable from the known reactants and observable data, the quantity Q_{χ} computed from $Q^* - Q_E^*$ can be regarded as a function of the parameter ϵ_m . In principle then, there should only be one value of ϵ_m ; i.e., the true value of ϵ_m , for which the plot of $\tau(Q_{\chi}^*)$ against t_{χ}/R^2 is straight. The slope of this line will be the true diffusivity, α_m , of the gas mixture at the moment of peak pressure. This is illustrated schematically in. Fig. 14. It remains to be seen whether, in practice, the accuracy of pressure-time traces will allow a procedure of this type to be carried to completion.

3. Description of Apparatus

In view of the potentialities of the explosion techniques, it was decided to conduct a series of preliminary explosion experiments for the purpose of gaining familiarity with the procedure and with the requisite instrumentation. While a spherical enclosure would have been desirable for direct applicability of the theory of conductive and radiative heat loss, the more limited objectives above could best be served by making use of a cylindrical vessel which was available at the time and which

was easily modified to meet the experimental requirements of strength and accessibility.

The apparatus required for a complete experiment can best be broken down, for descriptive purposes, into four categories:

- 1) the explosion vessel itself,
- 2) a filling (loading) system,
- 3) transient pressure instrumentation, and
- 4) transient heat flux instrumentation.

Several features of each of these systems are discussed below. This will be followed by a summary of the results obtained to date and an outline of possible improvements in the experimental technique.

a. The Explosion Vessel. The vessel itself consisted of a modified cylindrical reactor of stainless steel construction. Originally, this vessel had an interior depth of 24 cm and an internal diameter of 17.32 cm. The wall thickness was 3.02 cm. The head was sealed with a lead gasket and contained only a rupture disc at its midpoint. The vessel as used in the experiment differed from the original in the following respects (see Fig. 15). First, the lead gasket was replaced by an O-ring (Dash No. 440) seal. The interior dimensions of the vessel were altered by the addition of a cylindrical insert designed to leave a cavity whose depth was equal to its diameter (17.32 cm). It is readily verified that such a cylinder has the same surface to volume ratio (6/d) as an inscribed sphere of the same diameter. Fastened to this insert was a 0.159 cm diameter stainless steel electrode (E_2) which reached up to the center of the cavity. The other electrode (E_1) consisted of a similar rod which extended horizontally from the center of the bomb to the centerpost of an 18 mm automobile spark plug (S) mounted in the sidewall of the vessel. Since it was decided to use the center hole in the cover for a transient heat flux gauge (T) (to be described), three further holes had to be machined into the vessel walls, i.e., provision for the pressure pickup (P), gas inlet and exhaust (IE) and condensate drainage (D). The first two of these were added to the cover. The latter was machined in the base of the bomb. Electrically, the bomb itself was grounded and the ignition was accomplished by passing a spark across the centrally located electrode gap. For this purpose, two distinct energizing techniques have been used, the first of which made use of a standard automobile induction coil. The second made use of a capacitor discharge. In each case, completion of the ignition circuit was used to trigger the sweep of the oscilloscope on which the pressure and heat flux traces were recorded.

b. The Filling (Loading) System. The system used for loading and evacuating the explosion vessel is shown schematically in Fig. 16. Apart from a series of valves, its main components are a pressure gauge (at D), a vacuum pump (at E) and the fuel-oxidizer supply tanks (at C).

The loading procedure adopted is as follows. With valves 1 through 6, all open, the entire system, including the pressure vessel, is first evacuated and the pressure recorded. The shut-off valve 4 is then closed, isolating the vacuum pump from the remainder of the system. At this point, the regulator valve on gas bottle 1 is opened, and this gas is admitted into the system until some predetermined pressure level is reached. When the solenoid valve 6 is closed, this gas is then trapped inside the bomb. By opening valve 4, the filling system is once again evacuated, to make ready for the escape of gas 2. Valve 4 is then closed, and the regulator valve on gas bottle 2 is opened to admit this gas into the filling system. The normally closed solenoid valve (6) is then energized and closed when the pressure in the bomb and filling system is slightly in excess of the desired initial value. The filling system is again evacuated by reopening valve 4. The metering valve (5) may then be used to bleed off small amounts of gas to approach the desired starting pressure p, provided that enough time is allowed for the mixing of reactants in the vessel[†]. When the filling system is again re-evacuated or filled with air, the bomb is ready for ignition, subject to the additional requirement. A knowledge of the barometric pressure, vessel temperature, and pressures after the addition of reactants 1 and 2, as well as after the bleed period, enable the determination of both the total mass input and the mixture ratio. Provision can also be made for the addition of diluent gases, if desired,

c. Transient Pressure Instrumentation. Commercially available strain gauge pressure pickups were used to obtain the pressure-time history of the gases in the bomb. These pickups were threaded into the bomb cover to a depth such that the pressure sensing surface was flush with the interior of the vessel. Records have been obtained thus far with two distinct pickups. The first of these was a Dynisco Co. PT 31-2M, O - 2000 psi unbonded strain gauge with a 1/4 inch diaphragm and 17000 cps resonant frequency. This gauge was supplied with a 6 volt dc input (excitation) and had an experimentally determined sensitivity of 98.1 psi per millivolt in the pressure

At the largest loading pressures contemplated (125 psia), the calculated mixing time for a hydrogen-oxygen mixture is about 30 minutes, based on molecular diffusion alone.

[‡]Dynamic Instrument Company, Cambridge, Massachusetts

range up to 300 psia. The second pressure pickup used was a Dynisco Model PT 76B-1M strain gauge with an intended range of 0 - 1000 psi. The nominal full range sensitivity of this gauge was 2.99 millivolts per 1000 psi per volt excitation. At 6 volt excitation this corresponded to 55.5 psi/mv. Because of the differences in construction between the aforementioned gauges, it was anticipated that the second would be less affected by mechanical oscillations in the vessel walls.

d. Transient Heat Flux Instrumentation. If it is possible to record the temperature-time history $T_w(t)$ of a thick material of known thermal diffusivity, a_w , then the instantaneous heat transfer rate $\dot{q}''(t)$ to this surface can be computed from the well-known relation⁴⁷

$$\dot{q}''(t) = \frac{\lambda_w}{\sqrt{\pi}} \int_0^t \frac{1}{\sqrt{\alpha_w \cdot (t - t')}} \left[\frac{dT_w}{dt'} \right] dt'$$
 (26)

Since an independent knowledge of the instantaneous <u>local</u> heat flux is desirable, two fast response surface temperature recording methods have been investigated, with only marginal success. The first of these (see Fig. 17) made use of a thin film (F) of platinum painted on a quartz backing plate (Q). The change in the resistance of this film was then used to determine the instantaneous surface temperature of the quartz, as outlined in Ref. 48 and 49. The second method made use of a commercially available "surface thermocouple" probe⁵⁰. This latter probe, supplied by the Nanmac Corporation, made use of a copper-constantan junction formed across a thin mica strip by polishing the sensing tip. While the response time of the thermocouple gauge is of the order of 10⁻² msec, the uncertain properties of the backing material make some kind of calibration process necessary, if absolute heat fluxes are desired.

4. Discussion of Preliminary Experimental Results

Experience with the instrumentation described above has more than justified our initial decision to postpone the construction of a spherical vessel pending the outcome of a series of preliminary experiments with the existing cylindrical vessel. Perhaps the most striking feature of the pressure-records, for stoichiometric explosions, are the high frequency oscillations ("hash") superimposed on the trace (see for example,

Type G "Pencil Probe"; Narmac Corporation, P.O. Box 8, Indian Head, Maryland

Fig. 18A). This particular record corresponds to the following initial conditions: $p_i = 2.81 \text{ atm, } (32.9\%0_2, \ 64.1\%H_2, \ 3\%"N_2").$

The gauge sensitivity is 55.5 psi/mv. Oscillations of this type occurred for both pressure pickups over the pressure range examined (p_i = 1 atm - 9 atm). The effect of diluents was not examined. Fig. 18B shows a filtered record for p_i = 2.95 atm, initial mixture: 33.4‰, 65.6‰, 1‰"N₂". The gauge sensitivity is 98.1 psi/mv. This trace clearly shows the general shape of the pressure rise and subsequent decay. The horizontal line on the far right is the asymptotic value of the pressure for long times. This asymptote is lower than p_i due to the volume change upon reaction and condensation of water vapor within the vessel. The quality of the unfiltered traces obtained thus far has not been adequate for the data reduction procedure outlined earlier. It appears that the oscillations can be suppressed by adding diluents to the initial mixture⁵¹. There is also evidence that the oscillation problem is minimized in spherical cavities. If the oscillations occur for stoichiometric mixtures in spherical cavities, then the need to add diluents would constitute a fundamental limitation of the experimental technique.

A large number of explosions were carried out to develop a thin film (platinum) resistance thermometer for making direct heat flux measurements. Hanovia paints were applied to quartz discs supplied by the Film Ohm Corporation. These discs were then inserted into a brass mount (see Fig. 17). The films were then soldered to a center-post terminal (T_1) and the mount itself (T_2) . Records obtained with these gauges showed two types of defect. First, many records exhibited a sharp spike superimposed on an otherwise reasonable resistance-time trace. Secondly, serious zero shifts in gauge resistance were observed from test to test. Experience to date suggests that the mount shown in Fig. 17 is unacceptable in that the quartz discs do not appear to be adequately supported and are thus subjected to physical strain during the course of the explosion. In addition, the method described above for making electrical contact with the platinum film proved to be unequal to the severe environment to which the soldered joints were exposed. However, if these mounting difficulties can be overcome, the resistance thermometer gauge would have much to recommend it over commercially available surface thermocouple gauges of the type described earlier.

Film Ohm Corporation, 48 W. 25th Street, New York 10, New York
These discs are used in the fabrication of microwave resistors. We are particularly
indebted to Mr. Charles Kc sman, of the Film Ohm Corporation, for his cooperation and
suggestions with regard to the use of the quartz discs.

Summary of High Pressure Program

The prospects for using constant volume explosions to determine energy transport properties of chemically reacting gases under conditions of extreme pressures and temperatures have been discussed and possible theoretical and experimental approaches to the problem have been outlined. In particular, by combining theoretical solutions for the energy transfer rate from a compressible, heat conducting and radiating sphere of gas to the confining vessel walls, with a relatively small number of experimental measurements (in the extreme case, transient pressure alone) it may be possible to extract both the thermal diffusivity and radiative emissivity of the enclosed gases. In view of the potentialities of the technique, a series of preliminary explosion experiments have been carried out using stoichiometric hydrogen-oxygen mixtures in a cylindrical vessel. The principal difficulties encountered in these experiments were the presence of high frequency pressure oscillations superimposed on the desired pressuretime decay ("cooling curve") and repeated failure of thin film heat transfer gauges exposed to the explosion products. The pressure oscillations observed in the present experiments may not be so severe in spherical cavities. Evidence also exists that they can be suppressed by the addition of diluents. The possibility of obtaining reliable heat flux traces will then depend upon improvements in the mounting of such gauges. Surface thermocouple gauges^{52,53}, of the type used in automotive practice have been investigated and appear to be free of this ruggedness problem. However, such gauges may be less accurate for heat flux measurements unless they are carefully calibrated in a known heat flux situation.

IV. CONCLUDING REMARKS

On the basis of the research carried out thus far, two potentially fruitful methods have been delineated for experimentally studying energy transfer rates in chemically reacting gases under extreme conditions of pressure and temperature. Preliminary results have been given both for chemically reacting ethylene/oxygen and hydrogen/oxygen in the pressure range 5 - 15 mm Hg as well as for hydrogen/oxygen explosions at pressures up to 1000 psia. It is hoped that the present work will stimulate further investigation along the lines proposed, with perhaps a greater awareness of the potential pitfalls, both experimental and theoretical. "... the subject is a fair field for the struggle to gain knowledge by scientific reasoning; and, win or lose, we find the joy of contest".

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APPENDIX 1 - THERMAL AND PHYSICAL PROPERTIES OF MERCURY

Two short tables of several useful heat transfer properties of mercury are included here for convenience. The data include density, specific heat, thermal conductivity, absolute viscosity, volumetric heat capacity, thermal diffusivity, kinematic viscosity and Prandtl number for heat conduction over the temperature range 0 to 250°C, at atmospheric, or near-atmospheric, pressure.

TABLE IV

HEAT TRANSFER PROPERTIES[‡] OF MERCURY

Density, Specific Heat, Thermal Conductivity and Absolute Viscosity at Total Pressures Near Atmospheric

T ^o C	ρ	c _p	100 λ	μ	т ^о к
0 20 40 60 80 100 200 250	13.60 13.55 13.50 13.45 13.40 13.35 13.11 13.00	0.03346 0.03325 0.03308 0.03294 0.03284 0.03269 0.03230 0.03210	1.96 2.09 2.20 2.31 2.42 2.51 2.96	1.68 1.55 1.44 1.35 1.27 1.21 1.01 0.96	273 293 313 333 353 373 473 523

Liquid Metals Handbook, Second Edition, Government Printing Office, Washington, D.C., 1952; see also Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, Cleveland, Ohio

[‡]Units are as follows: density in gm(cm)⁻³; specific heat in cal(gm)⁻¹(O K)⁻¹; thermal conductivity in (cal)(cm)⁻²(sec)⁻¹(O K/cm)⁻¹; absolute viscosity in gm(cm)⁻¹(sec)⁻¹

TABLE V

HEAT TRANSFER PROPERTIES OF MERCURY

Volumetric Heat Capacity, Thermal Diffusivity, Kinematic Viscosity and Prandtl Number at Total Pressures Near Atmospheric

T ^O C	ρc _p	α	ν	$^{\mathtt{Pr}}\!\lambda$	$(Pr_{\lambda})^{\frac{1}{2}}$	т ^о к
0	0.4549	0.0431	0.00124	0.0287	0.169	273
20	0.4504	0.0464	0.00114	0.0246	0.157	293
40	0.4465	0.0493	0.00107	0.0216	0.147	313
60	0.4430	0.0522	0.00100	0.0192	0.139	333
80	0.4401	0.0549	0.000949	0.0173	0.132	353
100	0.4365	0.0576	0.000906	0.0157	0.125	373
200	0.4236	0.0698	0.000770	0.0110	0.105	473
250	0.4172	• • •	0.000739	• • •	• • •	523

Units are as follows: volumetric heat capacity in cal(cm)⁻³($^{\circ}$ K)⁻¹; thermal diffusivity and kinematic viscosity in (cm)²(sec)⁻¹; Prandtl number, dimensionless

APPENDIX 2 - EFFECTS OF WATER VAPOR CONDENSATION ON THE EXPLOSION METHOD

Condensation of water vapor is one of the causes of variations in the specific heat, c., during the cooling process. Moreover, the diffusion of water vapor to the cold wall, where it condenses exothermically, constitutes a potentially important energy transfer mechanism other than ordinary heat conduction. This results in the well-known calorimetric concept of "higher" and "lower" heating values for fuels containing hydrogen; i.e., each fuel will have two heating values, which will differ by the product of the latent heat of vaporization, H, and the total mass of water formed by condensation in the vessel. With regard to use of an explosion method for deducing gas phase thermal diffusivities, it is intuitively clear that if the difference between the higher and lower heating values of the combustible is negligible compared to the absolute value of the lower heating value, then the effect of water vapor condensation on the inferred thermal diffusivity will necessarily be small. If the condensation occurs mainly at the walls themselves, then the fact that the Fick diffusivity $D_{\mbox{H}_2\mbox{O-mix}}$ is generally less than the thermal diffusivity α of the gas mixture would further contribute to the relative importance of energy transport by ordinary heat conduction. This is particularly clear in the case of diffusion controlled vaporization for short times, since the square root law $(Q_{\chi} \propto \sqrt{ au})$ immediately leads to the conclusion that, up to any time t, the ratio of the total heat \mathbf{Q}_{D} (liberated as a result of water vapor diffusion and condensation) to $Q_{\pmb{\lambda}}$ is given by

$$\frac{Q_{D}}{Q_{\lambda}} \cong \left[\frac{D_{H_{2}O-mix}}{\alpha_{mix}}\right]^{\frac{1}{2}} \frac{Q_{D}(\infty)}{Q_{\lambda}(\infty)}$$

For longer times, droplets probably form on the wall. These droplets would increase in size until gravity would force them to run down the wall. On clean surfaces continuous films are also possible. In both cases, the presence of water at the surface introduces an additional resistance for the flow of heat to the wall. Only in certain extremely simple cases are the laws governing heat transfer in this type of environment theoretically understood (see, for example, Chapter 12 of Eckert and Drake⁴⁰). It is also clear that the effective radiative absorptivity of the vessel walls is likely to change as condensation proceeds. For these reasons, unless this process can be artificially inhibited (delayed), the accuracy of the explosion method as a means of determining gas phase transport properties is expected to degenerate in the presence of large amounts of condensation.

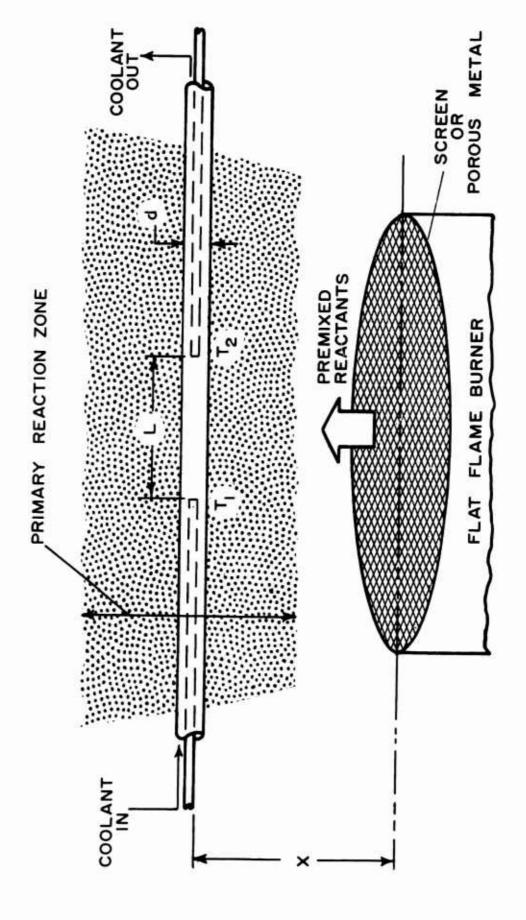


FIG. 1 CONFIGURATION OF BURNER AND HEAT TRANSFER PROBE (SCHEMATIC)

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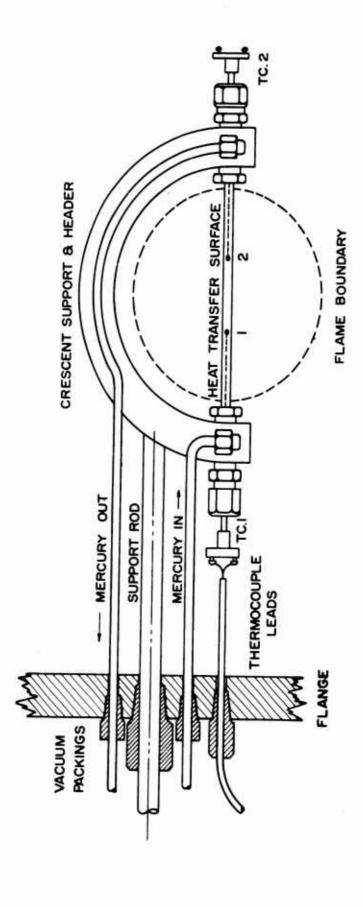


FIG. 2 PLAN VIEW OF MERCURY COOLED HEAT TRANSFER PROBE (SCHEMATIC)

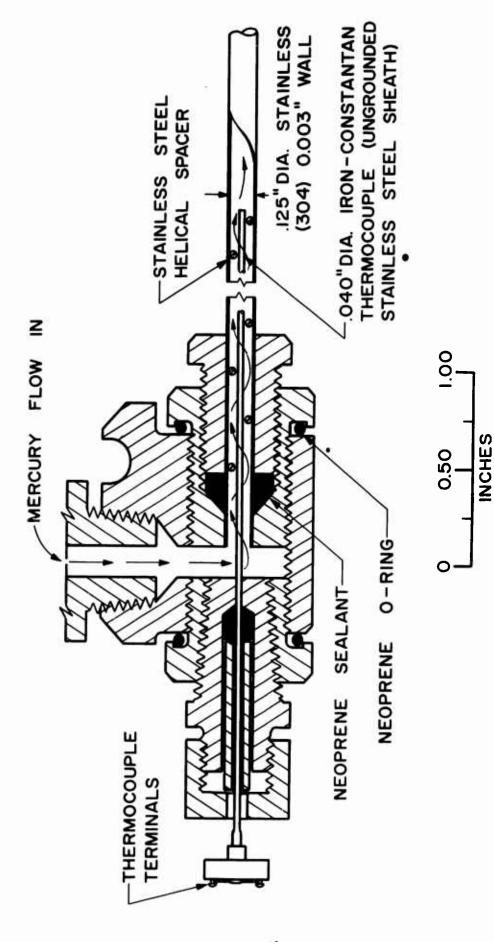
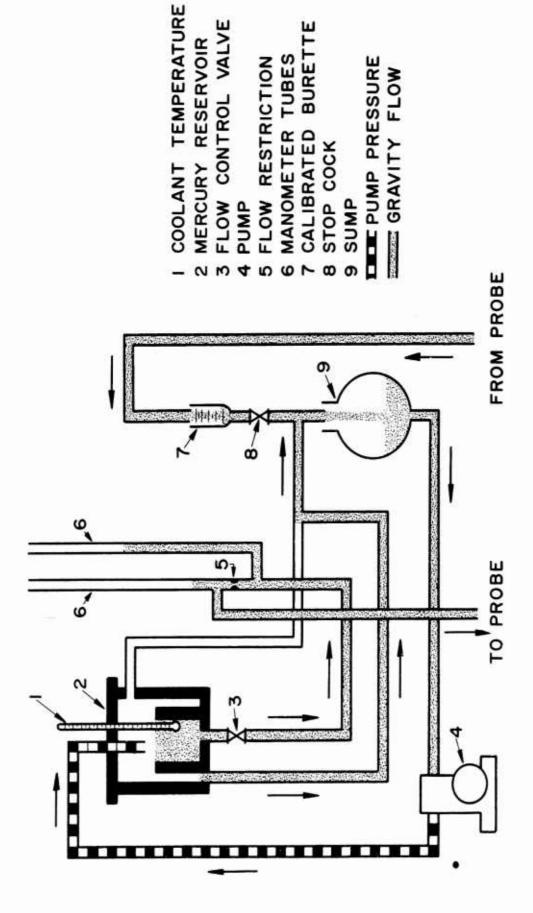


FIG. 3 CROSS-SECTIONAL DETAIL OF PROBE THERMOCOUPLE AND COOLANT FLOW CONFIGURATION (TO SCALE)



BURETTE

FIG. 4 CONSTANT HEAD MERCURY FLOW SYSTEM (SCHEMATIC)

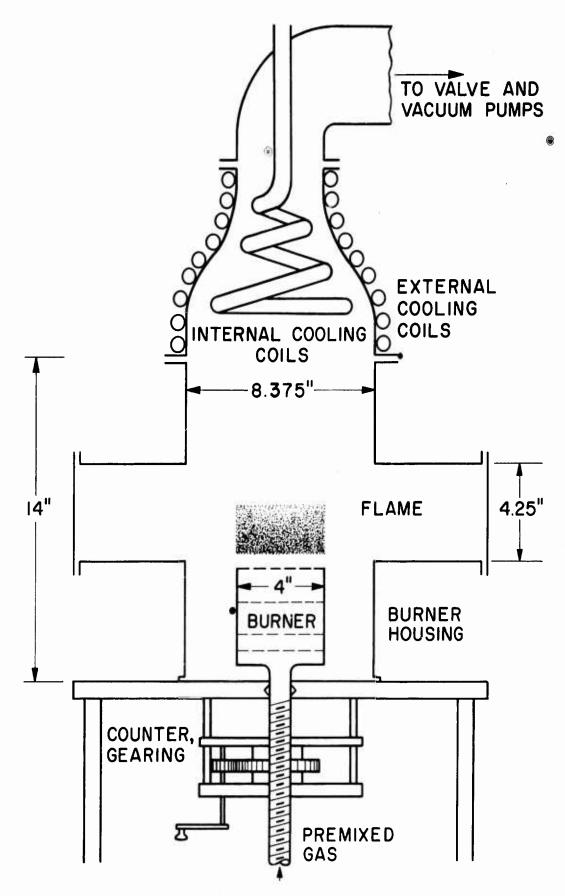


FIG. 5 SCHEMATIC OF LOW PRESSURE BURNER ASSEMBLY

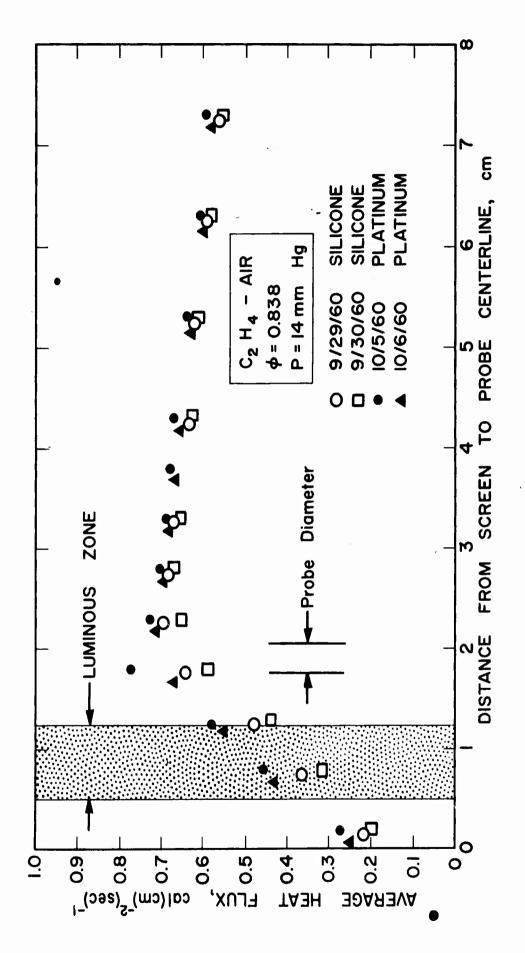


FIG. 6 HEAT FLUX AS A FUNCTION OF POSITION IN A LEAN ETHYLENE AIR FLAME

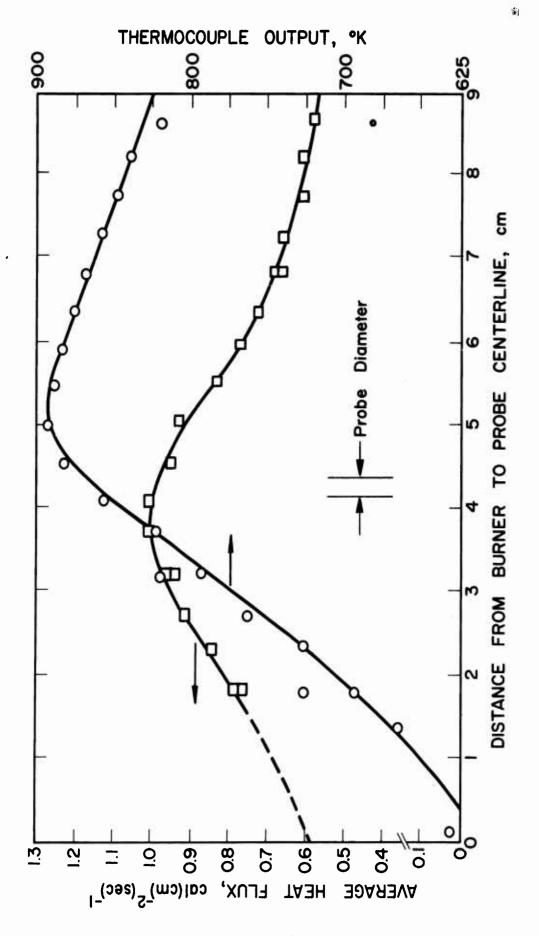


FIG. 7 HEAT FLUX AND RELATIVE TEMPERATURE AS A FUNCTION OF POSITION IN A RICH OXY-HYDROGEN FLAME

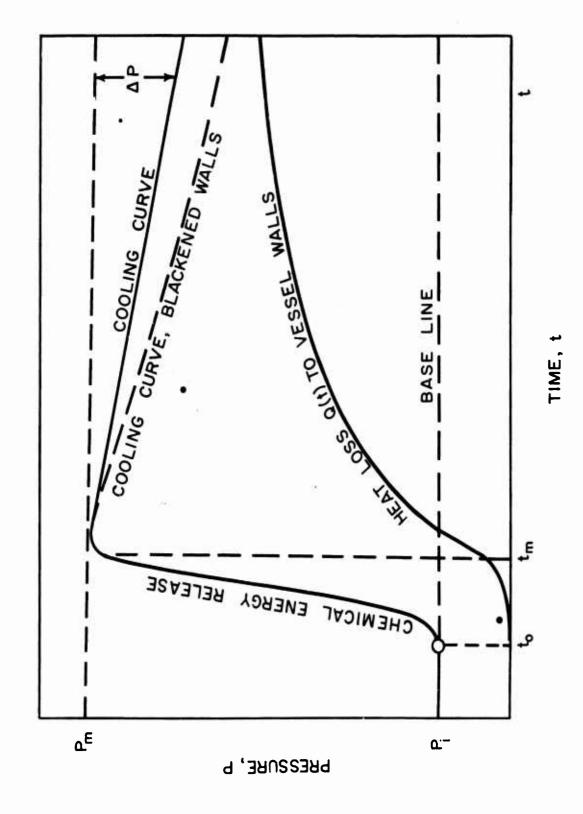


FIG. 8 TYPICAL TRANSIENT PRESSURE AND INTEGRATED HEAT LOSS RECORDS FOR A CONSTANT VOLUME EXPLOSION

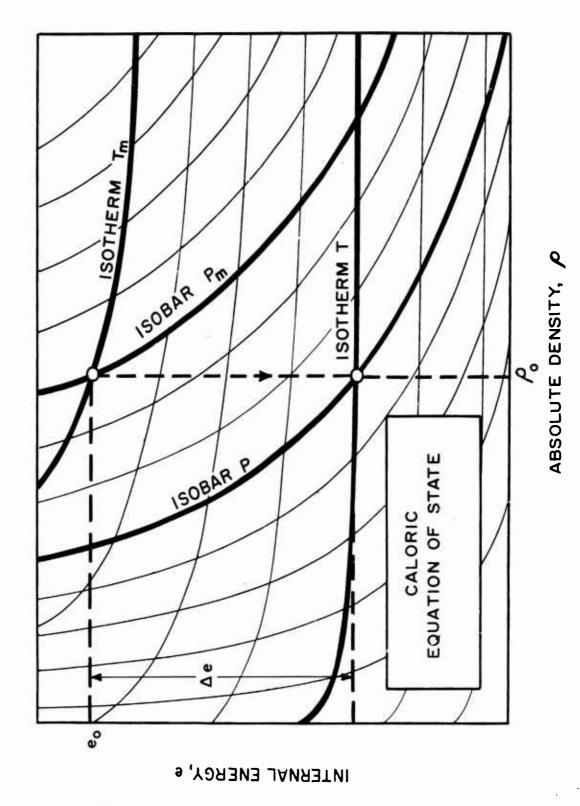


FIG. 9 COOLING PROCESS REPRESENTED ON THE INTERNAL ENERGY-DENSITY PLANE

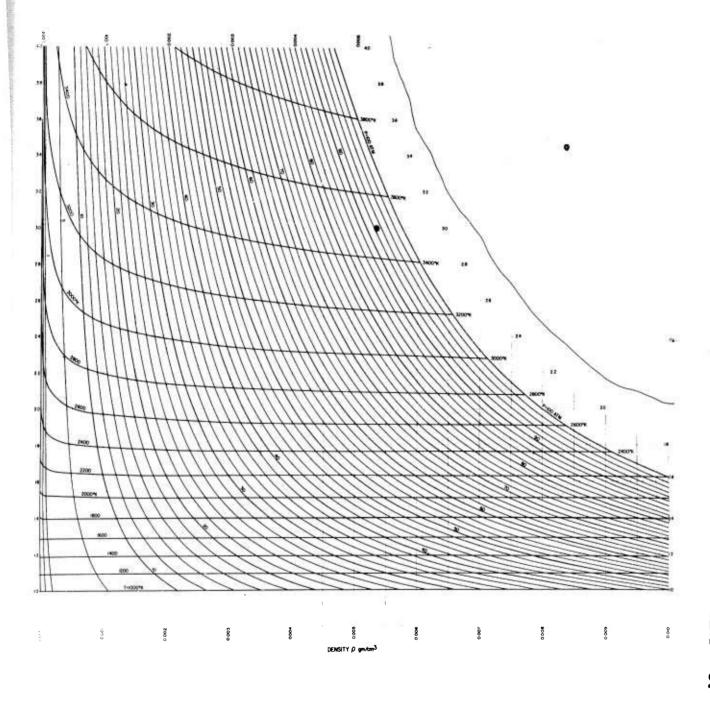


FIG. 10

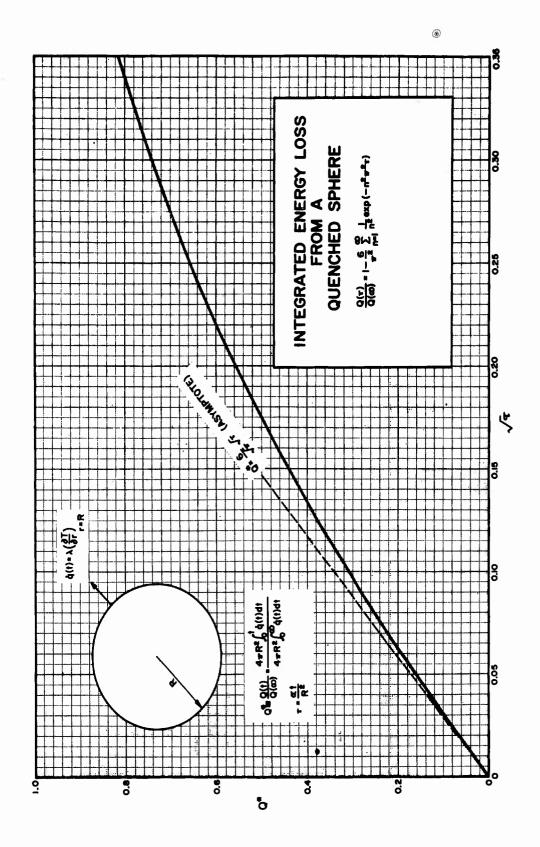


FIG. 11 DEPENDENCE OF NORMALIZED HEAT LOSS ON NONDIMENSIONAL TIME (FOURIER QUENCHED SPHERE SOLUTION)

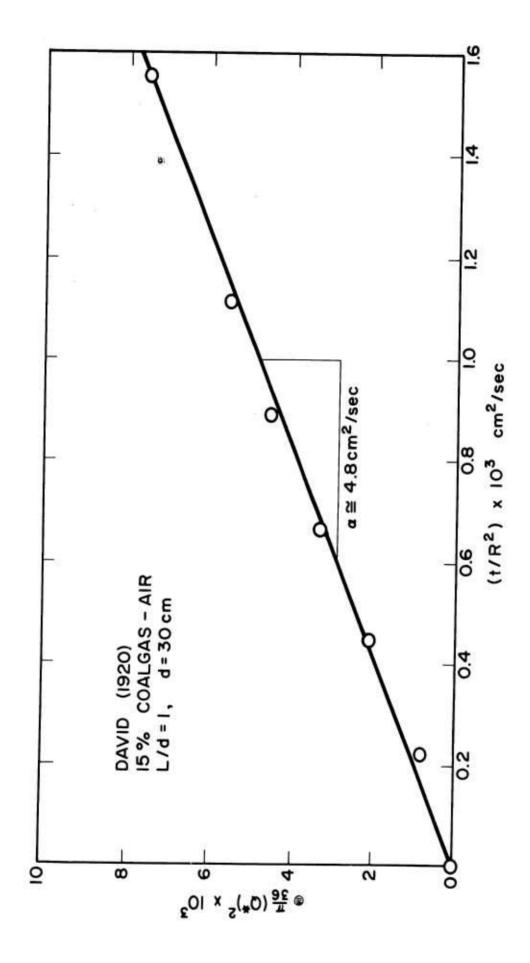


FIG. 12 GRAPHICAL DETERMINATION OF EFFECTIVE THERMAL DIFFUSIVITY FROM RELATIVE CONDUCTIVE HEAT LOSS MEASUREMENTS

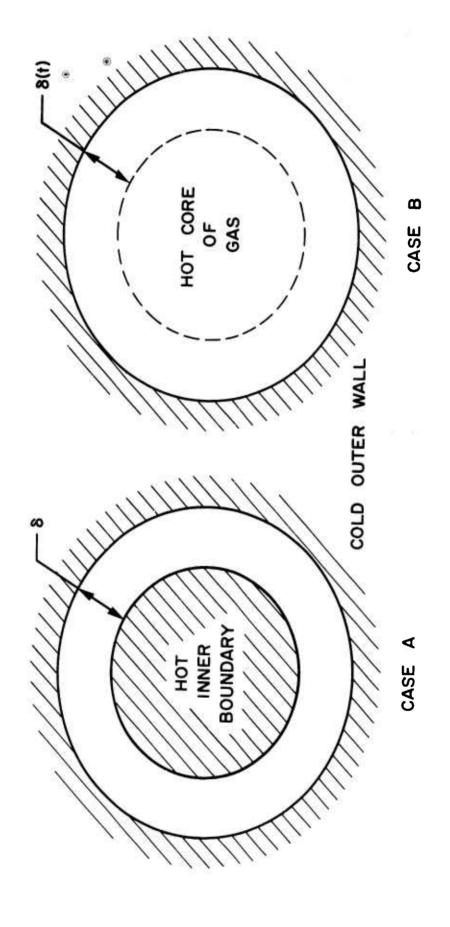


FIG. 13 FREE CONVECTION IN ENCLOSED SPACES

a

- STEADY-STATE, WITH INNER BOUNDARY TRANSIENT, WITH NO INNER BOUNDARY A .

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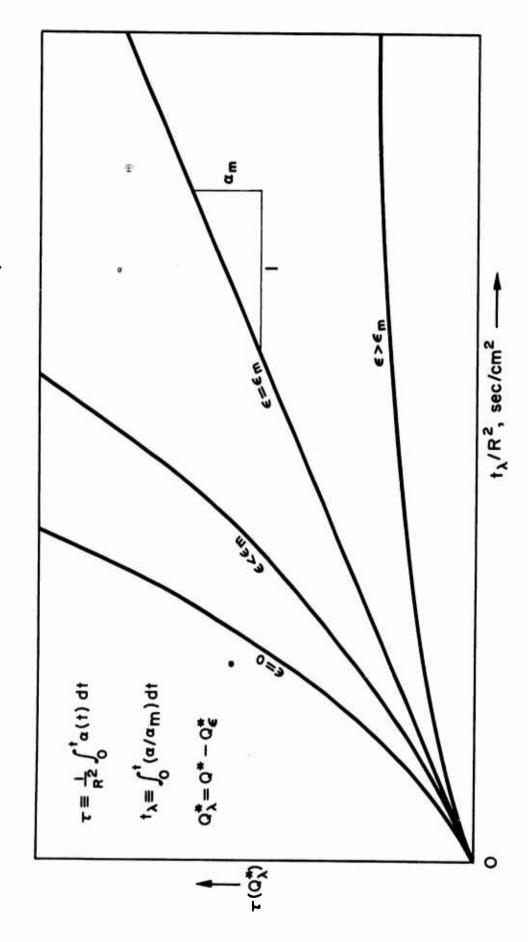


FIG. 14 GRAPHICAL DETERMINATION OF BOTH DIFFUSIVITY AND EMISSIVITY FIG. 14 GRAPHICAL DETERMINATION OF BOTH DIFFUSIVITY AND EMISSIVITY

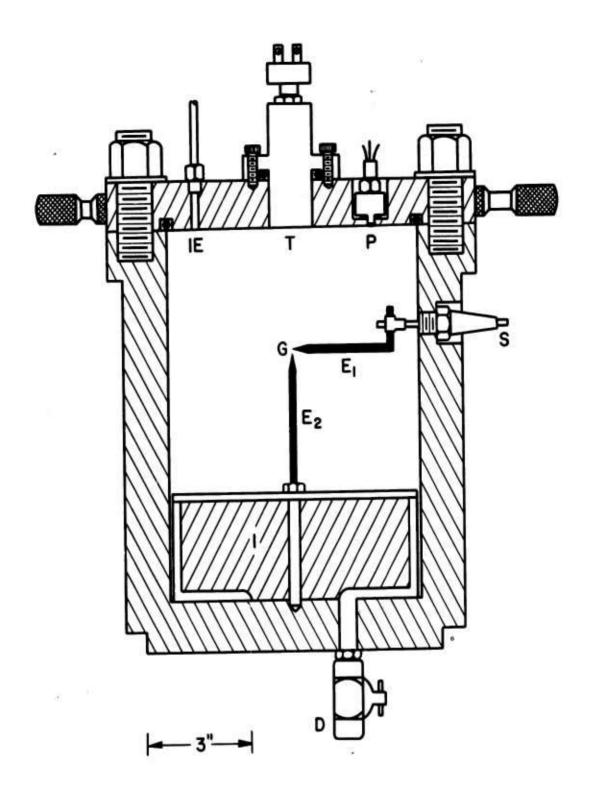


FIG. 15 SCALE DRAWING OF CYLINDRICAL EXPLOSION VESSEL

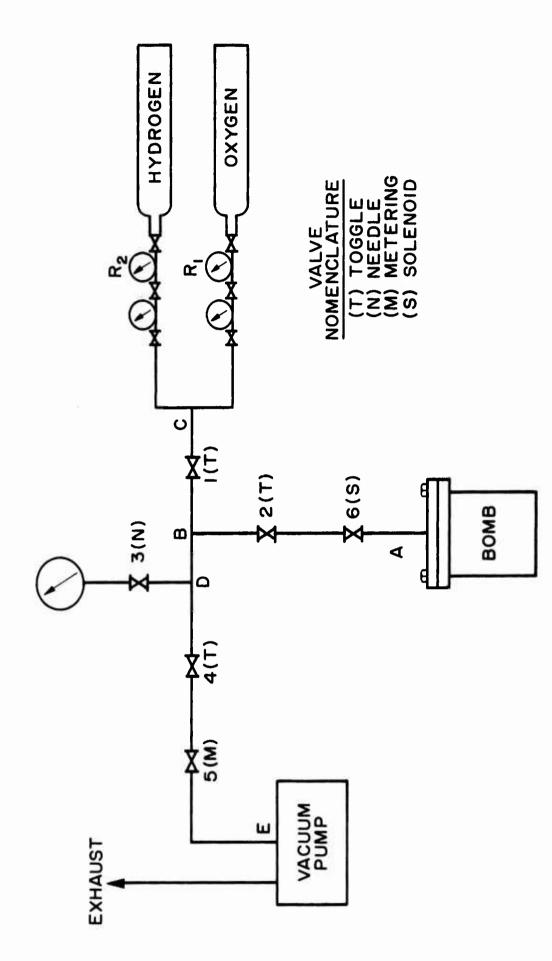


FIG. 16 EVACUATION AND LOADING SYSTEM

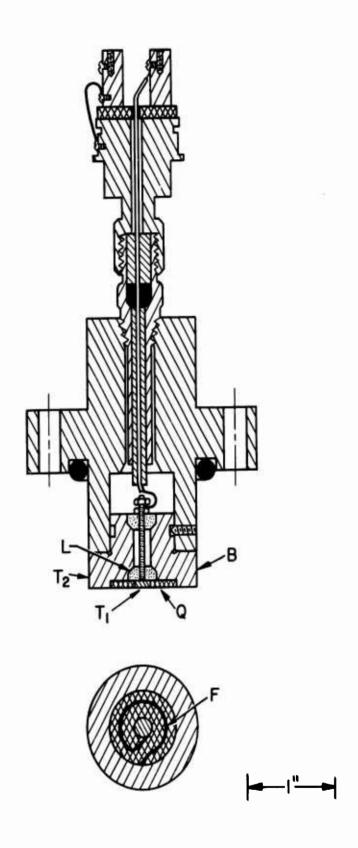
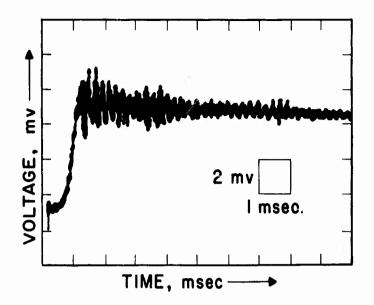
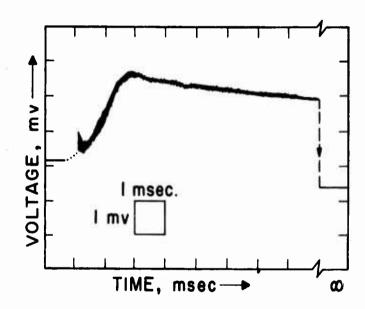


FIG. 17 CROSS-SECTION OF THIN FILM RESISTANCE THERMOMETER ASSEMBLY



A. Initial Pressure = 2.81 atm; Initial Composition = 32.9% 0_2 , 64.1% H_2 , 3% " N_2 "; Gauge Sensitivity = 55.5 psi/mv



B. Initial Pressure = 2.95 atm; Initial Composition = 33.4% O_2 , 65.6% H_2 , 1% " N_2 "; Gauge Sensitivity = 98.1 psi/mv

FIG. 18 PRESSURE PICKUP OUTPUTS AS A FUNCTION OF TIME

UNCLASSIFIED		UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED
	AeroChem Research Laboratories, Inc., Princeton, New Jersey, CONVECTIVE HEAT TRANSFER WITH CHEMICAL REACTION by Daniel E. Rosner. August 1961. 56 p. incl illus, tables. (Project 7013; Task 70179) (Contract AF 33(616)-6216). ARL 99, Part II. Unclassified Report	A novel method of measuring steady state heat fluxes to strongly cooled catalytic and non-catalytic solids within subatmospheric flames is described and used to obtain heat flux data as a function of position in flat ethylene/air and hydrogen/oxygen flames stabilized on a 4 inch diameter burner.	For determining energy transport properties of gases at pressures up to or exceeding 1000 psi, a constant volume explosion technique is introduced. Factors limiting the attainable accuracy of emissivity and thermal diffusivity determinations are quantitatively discussed. In view of the theoretical potentialities of the technique, a series of preliminary explosion experiments have been carried out using stoichiometric hydrogen/oxygen mixtures in a cylindrical vessel.	
UNCLASSIFIED		UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED
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UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED
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